MANGANESE DIOXIDE ELECTRODE WITH STABLE POTENTIAL.

PART II. STRUCTURAL INVESTIGATIONS

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An investigation has been made for the reasons for the unusual electrochemical behavior of certain synthetic samples of manganese dioxide. Unlike the varieties usually employed, the samples investigated, even at early stages of cathodic reduction give discharge products in the form of a separate phase consisting of the heterolyte $ZnO \cdot Mn_2O_3$. The reason for this behavior of the dioxides investigated is not connected with the nature of the crystalline lattice, the presence of impurities, or other bulk properties of the samples. It has been found that the particles of these dioxides, unlike those usually employed, have a clearly developed tread-like form. The suggestion is made that surface properties of the dioxide play a decisive part in the phenomena investigated.

The cathodic reduction of a manganese dioxide electrode in alkaline and salt solutions is well known to be accompanied by a continuous fall in its potential. This fact reflects unfavorably on the properties of manganese elements, being revealed in a declining charge curve and a low exploitation coefficient for manganese dioxide. These properties are determined by the solid-phase reduction of manganese dioxide, which leads to the formation of a phase of variable composition, consisting of a solid solution of products discharged into the initial manganese dioxide [1-4].

This mechanism for electrochemical reduction has been confirmed experimentally using samples of manganese dioxide, used at the present time in industry, including pyrolusite, GAP, electrolytic γ-MnO_2, and others. We have synthesized manganese dioxide in a form corresponding to the so-called ρ-modification, which was found to show a stable discharge potential, and practically 100% exploitation when used as cathode in elements operating in a salt electrolyte [5]. The results of the electrochemical investigations we have carried out are in good agreement with the suggestion that, under conditions of discharge in a small volume of electrolyte, this dioxide (unlike the types normally used) has no tendency to the formation of a phase of variable composition. Hence, even at comparatively early stages of discharge a compound containing tervalent manganese is formed as a separate phase. It has been shown that right at the beginning of the cathode process, using this sample of dioxide, its kinetics are determined by difficulties associated with the formation of the new phase [6].

However, even in the earlier work [5, 6], facts were produced which indicate clearly the unsatisfactory nature of this explanation. It was shown that the synthetic γ-MnO_2 obtained by thermal treatment of ρ-MnO_2 also possesses unusual properties similar to the initial ρ-MnO_2 itself. At the same time x-ray investigations indicate that the sample does not differ from electrolytic γ-MnO_2 or from GAP, which gives a phase of variable composition and declining charge curves. A similar difference was observed in the properties of synthetic β-MnO_2, also obtained from ρ-MnO_2, in comparison with pyrolusite: although the x-ray diagrams were identical, the discharge curve for the former was horizontal, and for the latter declining.

To elucidate the cause for this contradictory behavior we have carried out more detailed structural investigations of the dioxides obtained, and of their reduction products.

EXPERIMENTAL

a) Initial products. Synthetic ρ-, γ-, and β-manganese dioxide were prepared according to the method described earlier [5]. For comparison experiments were conducted in parallel on the so-called GAP (γ-MnO_2), electrolytic γ-MnO_2, and pyrolusite (β-MnO_2).

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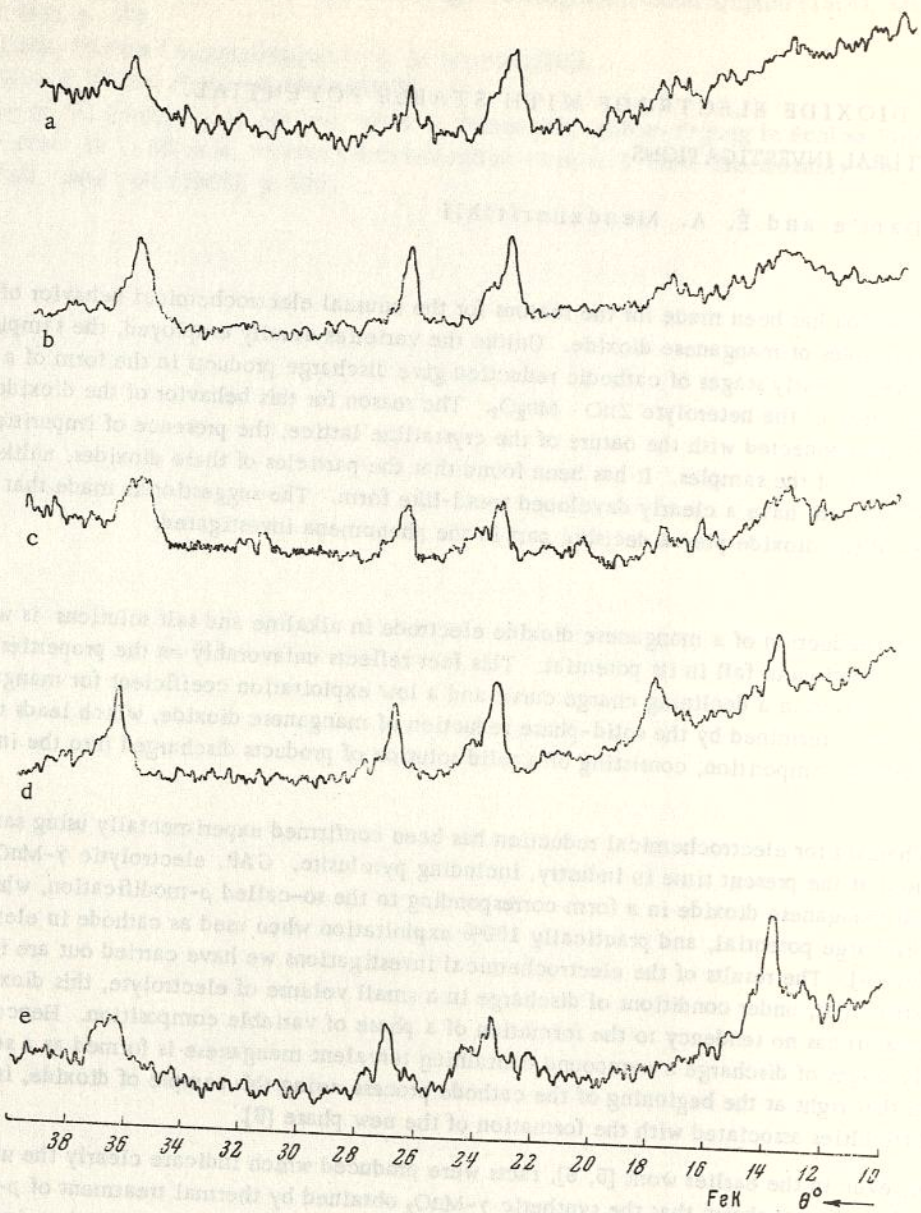


Fig. 1. X-ray diagrams of manganese dioxide: a) synthetic γ-MnO_2; b) electrolytic γ-MnO_2; c) GAP (γ-MnO_2); d) synthetic ρ-MnO_2; e) pyrolusite (β-MnO_2).

The samples were identified by x-ray analysis. The x-ray diagrams were obtained using diffractometer URS 50, using FeK illumination. The diagrams obtained from the investigated samples of manganese dioxide are shown in Fig. 1.

It may be observed that x-ray diagrams of the synthetic manganese dioxides, compared with those for GAP, pyrolusite, and electrolytic γ-MnO_2, are characterized by a somewhat greater diffuseness and lower intensity of the lines.

The specific surface of the samples was determined by the BET method from the adsorption of nitrogen. Table 1 contains the data obtained. The manganese dioxide samples investigated, with the exception of pyrolusite, have practically identical values of the specific surface.

The shape and dimensions of the manganese dioxide particles were investigated using electron-microscope IEM (from Japan). Suspensions of the samples in an aqueous-alcoholic mixture were introduced on to a colodium substrate.

Figure 2 shows the electronmicrographs of synthetic ρ-MnO_2.

TABLE 1. Specific Characteristics of Manganese Dioxide Samples

Type of manganese dioxide	Specific surface, m^2/g	Specific resistance (ohm · cm) when p = 3 T/cm^2	Specific gravity, g/cm^3
γ-MnO_2 synthetic	–	339	3.62
ρ-MnO_2 synthetic	44-47	12.48	3.40-4.20*
γ-MnO_2 synthetic	–	–	3.70-3.82*
β-MnO_2 electrolytic	38	16.9	4.39
GAP	48	516	4.21
Pyrolusite	11	15.73	4.62

* For samples from different batches.

It is seen from Fig. 2 that crystals of ρ-MnO_2, as well as the remaining synthetic samples, have a clearly developed thread-like form. Particles of GAP, pyrolusite, and electrolytic γ-MnO_2 are, however, practically shapeless aggregates of fine isotropic particles.

The density of manganese dioxide was determined by a pyknometric method in toluene. The data obtained are shown in Table 1. Synthetic samples show a lower specific gravity than GAP, pyrolusite, and electrolytic γ-MnO_2.

The differences between the dioxide samples in their tendency to the formation of solid solutions with their reduction products might in principle be capable of elucidation through thermographic and thermogravimetric experiments. Preliminary investigations have shown that these methods do not, however, show any major differences in this respect, even amongst samples as different in structure and electrochemical behavior as ρ-MnO_2 and GAP. For this reason, the use of these methods was discontinued.

Structural investigations of manganese dioxide were carried out by measuring their specific electric resistance. This was determined by a sonic method, since other methods proved inaccurate because of the inclusion of a contact resistance in the measured values, which was of the same order as the resistance of the samples themselves. Table 1 gives data on the specific resistance of various samples of manganese dioxide, and the figures show that the synthetic dioxides have no superiority over the samples normally employed in this respect.

b) Discharge products. To elucidate the composition of phases formed on the electrochemical reduction of various types of manganese dioxide, recourse was had to polarographic and x-ray structural methods.

Manganese-zinc elements after discharge were opened up, and the positively active mass was repeatedly treated with anhydrous acetone until all the salt was removed. The choice of acetone instead of water for the washing process was made to prevent hydrolysis of the zinc chloride forming part of the electrolyte. The washed mass was dried in air and then dissolved with heating in hydrochloric acid (1 : 3). The solution so obtained was examined using an oscillographic polarograph IC-1 to determine the quantity of zinc. The half-wave potential of zinc was −1.06 V. Figure 3 shows the quantity of zinc in the positive electrode prepared from ρ-MnO_2 for various degrees of discharge. For comparison, a theoretical curve, calculated on the assumption of the formation of the heterolyte $ZnO \cdot Mn_2O_3$ on electrochemical reduction of manganese dioxide is also given. The experimental curve agrees with the theoretical one in the portion of the curve corresponding to a stable discharge potential. In the part correspond-

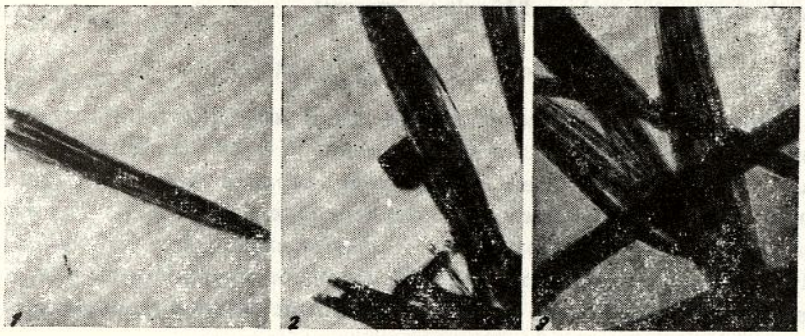


Fig. 2. Electron-microscopic photographs of synthetic samples: 1) γ-MnO_2 × 4100; 2) β-MnO_2 × 31000; 3) ρ-MnO_2 × 65000.

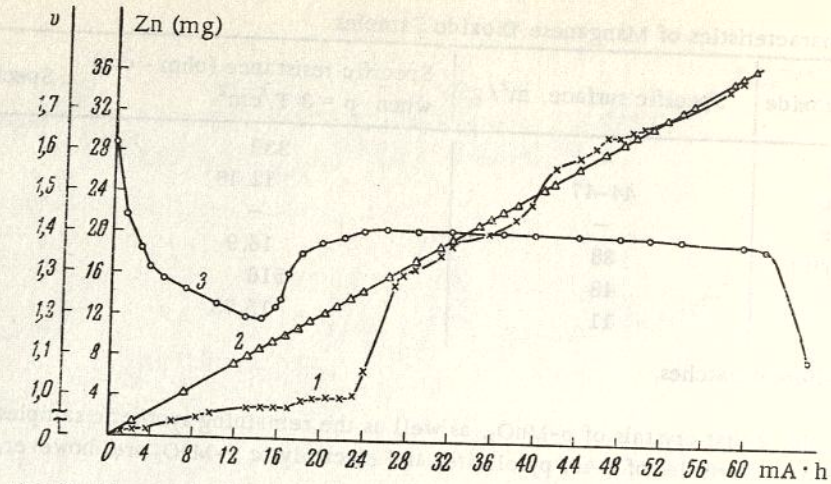


Fig. 3. Change in the zinc content in manganese dioxide electrode at various stages of discharge: 1) experimental quantity of zinc; 2) theoretical quantity of zinc, calculated on the assumption of the formation of a heterolyte; 3) discharge curve when I = 0.4 mA/cm².

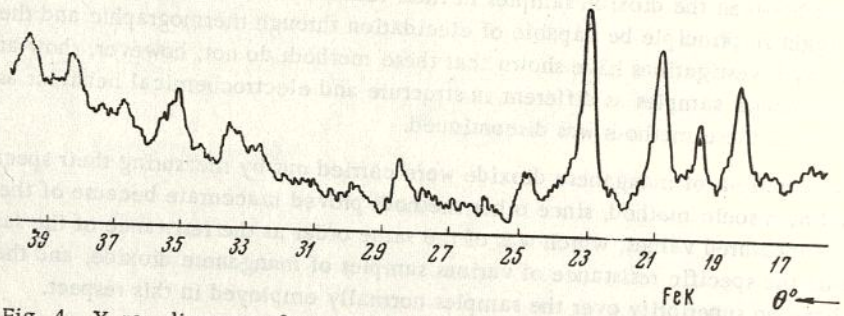


Fig. 4. X-ray diagram of the heterolyte obtained on discharge of synthetic ρ-MnO_2 for 63 mA · h.

ing to a dip in the discharge curve, zinc is detected in quantities less than theoretical. The result of x-ray structural analysis of the discharge products from ρ-MnO_2 are shown in Fig. 4.

For ρ-MnO_2, in the case of all the synthetic manganese dioxides, when discharge is taken to the dip point in the potential, the appearance of a heterolyte oxide phase is observed.

In the x-ray diagram of the final discharge product, there is no evidence of diffraction lines corresponding to the original dioxide, and the diagram corresponds entirely to the heterolyte [7, 8].

On discharge of GAP, pyrolusite, and electrolytic-MnO_2, a new phase is observed by x-ray analysis only at the end of discharge, when the potential at the element has dropped to a value smaller than 1 V. The x-ray diagrams of the final discharge products for these samples of manganese dioxide are quite different from those of the discharge products of synthetic samples, and are difficult to interpret.

DISCUSSION OF RESULTS

The structural investigations carried out confirm the initial assumption in [5] that on cathodic reduction of some types of synthetic manganese dioxides in a limited volume of a salt electrolyte, even at relatively early stages of discharge compounds of tervalent manganese are formed as a separate phase. Sufficient evidence has been found to justify the belief that this compound corresponds to the heterolyte $ZnO \cdot Mn_2O_3$. The dip in the discharge curve of the investigated samples of manganese dioxide (Fig. 3) may be explained by difficulties due to the formation of nuclei of the heterolyte. After the removal of these difficulties, the potential of the elements remains unchanged throughout the entire discharge, owing to the fact that the discharge occurs without change in phase composition, according to the equation:

$$2MnO_2 + Zn \rightarrow ZnO \cdot Mn_2O_3.$$

The reason for this unusual behavior of the investigated dioxide samples, remains, however, unclear. The absence of a tendency to the formation of a phase of variable composition with the reduction products would be expected to be connected with peculiarities in the crystalline structure of these dioxide samples. The experiments carried out, however, contradict this conclusion. Indeed we may state that the parameters which characterize the bulk properties of the particles of the investigated dioxides, from x-ray diagrams, electrical conductivity, NMR spectra, and other indications, do not differ from the corresponding values obtained from those types of manganese dioxide which are used in industry. The only exception to this is the specific gravity, which may be associated with complications in the experimental methods and also with differences in the water content and in impurities. An essential difference between the groups of dioxides considered may be observed by means of electron-microscopy. The fibrous, thread-like shape of the particles of the synthetic dioxides is quite different from the externally bounded particles of the second group of dioxides, and this may result in definite differences in the surface properties, and as a consequence, to the ion-exchange properties. The latter may be of considerable importance in determining the nature of the electrochemical process taking palce, which is confirmed by data which we have obtained, and which will be published subsequently in this series of papers.

LITERATURE CITED

1. P. D. Lukovtsev, Dissertation of the Institute of Physical Chemistry of the Academy of Sciences of the USSR [in Russian], Moscow (1952).
2. W. C. Vorsburgh, J. Electrochem. Soc., 106, 839 (1959).
3. J. J. Coleman, Trans. Electrochem. Soc., 90, 545 (1946).
4. J. Gabano, B. Morignat, and J. Laurent, Communication to 14th Conference of TsITTsE, Moscow (1963).
5. V. N. Dam'e and É. A. Mendzheritskii, Collection: Protective Metallic Coatings, Corrosion of Metals and Investigations in the Field of Electrochemistry [in Russian] (1965), p. 320.
6. V. S. Bagotskii and É. A. Mendzheritskii, Dokl. Akad. SSSR, 142, 127 (1962).
7. V. I. Mikheev, X-ray Structural Analysis of Minerals [in Russian], Gosgeoltekhizdat (1957).
8. L. C. Copeland and F. S. Griffith, Trans. Electrochem. Soc., 89, 495 (1946).